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Ultrafast energy and electron transfer in donor-acceptor molecules for photovoltaics

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J.-S. Lee, and J.-J. Kim, "The induced chirality in a polyisocyanate film and the polarization rotation change under an external electric field", *J. Opt. Soc. Am. B* (In press).

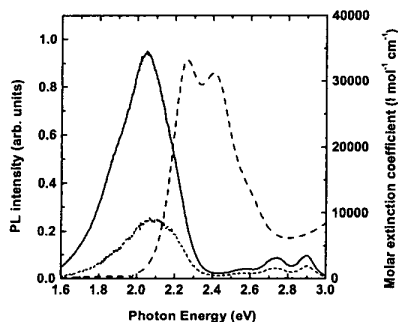
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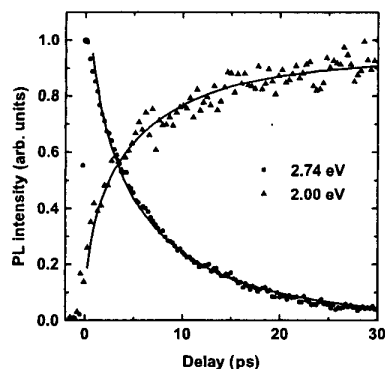
Influence of chain packing on the excitation transfer in perylene-end-capped polyindenofluorene

Laura M. Herz, Carlos Silva, Richard H. Friend, Richard, T. Phillips, Sepas Setayesh,* Klaus Müllen, *Cavendish Laboratory, Madingley Road, Cambridge, CB3 0HE, U.K.; *Max-Planck-Institut für Polymerforschung, Ackermannweg 10, D-55128 Mainz, Germany; Email: lmh33@cam.ac.uk

We have investigated the excitation transfer in a novel polymer/dye system consisting of the blue-



CMM5 Fig. 1. Molar extinction coefficient spectrum of a polyperylene derivative in chloroform solution (dashed line), together with the PL spectrum of perylene-end-capped PIFTEH for detection polarization parallel to the excitation polarization ($I_{||}$, solid line). The dotted line represents the PL difference spectrum ($I_{||} - I_{\perp}$) between the emission with polarization parallel and perpendicular to the excitation polarization and shows clearly the partly polarized emission from PIFTEH aggregates in the red (1.8–2.3 eV).



CMM5 Fig. 2. Time-resolved PL transients from perylene-end-capped PIFTEH showing the PL decay from PIFTEH chains (2.74 eV) and a corresponding rise in the red PL from the perylene end caps (2.0 eV) together with fits based on Förster theory.

light-emitting conjugated polymer poly(6,6'-12,12'-tetra-2-ethylhexyl-2,8-indeno[1,2-b]fluorene) (PIFTEH) as a host and red-light-emitting perylene molecules covalently bonded to the PIFTEH chain ends as a guest. The spectral overlap between the host emission and the guest absorption leads to an efficient Förster excitation transfer,¹ such that photo-excitation of the host results in emission originating predominantly from the guest (see Fig. 1). Using femto-second time-resolved photoluminescence (PL) spectroscopy, we find that the transfer of excitations from isolated PIFTEH chains to perylene molecules is completed within the first 30–40 ps after excitation, and we extract a Förster radius of (1.8 ± 0.3) nm from fits to the PL transients (Fig. 2).

We have modelled the polarization anisotropy for a guest-host system subject to Förster interactions using a Monte Carlo simulation and find that the emission from the guest becomes unpolarized at sufficiently high guest concentrations, even if the host emission displays a significant polarization anisotropy due to excitation with linearly polarized light. These results allow the separation of two overlapping contributions to the film emission in the red spectral region: the luminescence from perylene molecules and from sites where the PIFTEH chains aggregate. We find that while spectral overlap calculations¹ predict a large transfer of excitation to perylene molecules from sites where the PIFTEH chains aggregate, no transfer is observed experimentally. We attribute this to chain packing effects within the film: at sites where aggregation effects are dominant, the PIFTEH chains will be closely packed and ordered to some extent,² prohibiting sufficiently close contact between the host (PIFTEH) and the guest (perylene). The influence of interchain interactions on the excitation transfer probability is an important factor in the design of highly efficient light-emitting diodes (LEDs) based on conjugated polymer host systems.

Our novel approach, to bond covalently the dye guest molecules to the host polymer has distinct advantages over dye doping, since it prevents the phase separation of the dye molecules and therefore reduces the probability of concentration quenching for the dye emission. By incorporation of various dyes with suitable emission wavelengths, full-colour displays based on a common polymer matrix may be realized.^{3,4}

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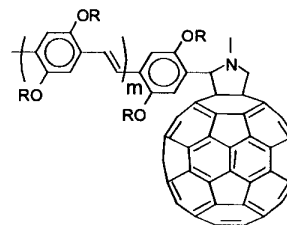
Ultrafast energy and electron transfer in donor-acceptor molecules for photovoltaics

P.A. van Hal, E. Peeters, B.M.W. Langeveld-Voss, R.A.J. Janssen, G. Lanzani,* G. Cerullo,* C. Gadermaier,* M. Zavelani-Rossi,* S. Desilvestri,* J. Knol,** J.C. Hummelen**, *Laboratory of Organic and Macromolecular Chemistry, Eindhoven University of Technology, P.O. Box 513, 5600 MB Eindhoven, The Netherlands; Email: r.a.j.janssen@tue.nl; *Istituto Nazionale per la Fisica della Materia, CEQSE-C.N.R., Dipartimento di Fisica, Politecnico, Milano (Italy); **Stratingh Institute and Materials Science Center, Groningen University, Nijenborgh 4, 9747 AG Groningen, The Netherlands*

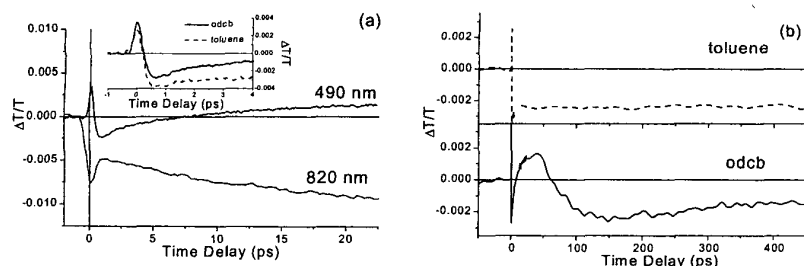
The rapid advancement in fullerene chemistry allows the covalent functionalization of C_{60} with electron donors. Various C_{60} -based donor-acceptor dyads have been synthesized and studied to gain insight in the *intramolecular* photophysical processes, like energy and electron transfer.^{1,2} Although these dyads can serve as a model compounds for the conjugated photovoltaic cells, only a few examples have been reported with these C_{60} -based dyads.^{3–5} Apart from being well-defined model systems for photophysical characterization, the covalent linkage between donor and acceptor in these molecular arrays provides a simple method to achieve control over the phase segregation in donor-acceptor networks. Here, we investigate an oligo(phenylene vinylene)-fullerene dyad with 4 phenyl groups (C_{60} -OPV₄) in solvents of different polarity using femtosecond pump-probe spectroscopy. We find that photoexcitation of the oligomer leads first to an intramolecular energy transfer to the fullerene, while an electron transfer is a secondary process, only allowed in polar solvents.

Pump-probe experiments with 200 fs time resolution are performed at 390 nm and single probe wavelengths are selected using interference filters after the sample. C_{60} -OPV₄ solutions ($\sim 2 \cdot 10^{-4}$ M) are excited mainly at the oligomer moiety.

After photoexcitation of C_{60} -OPV₄ in both toluene and in *o*-dichlorobenzene (odcb) at 390 nm, we observe at 490 nm first a positive signal due to a superposition of ground state bleaching and stimulated emission (SE) of OPV₄ as shown by the inset of fig. 2(a). This positive signal decays within 0.4 ps due to an ultrafast photoin-



CMM6 Fig. 1. The C_{60} -OPV₄ dyad, for $m = 3$.



CMM6 Fig. 2. (a) Differential transmission dynamics for C_{60} -OPV₄ in odcB (solid lines) and toluene (dotted line) on a 20 ps timescale (inset: 4 ps timescale) and (b) the same on a 400 ps at 490 nm.

duced. energy transfer to the fullerene moiety by which the photoinduced absorption (PA) $S_1 \rightarrow S_n$ band of C_{60} is obtained. Likewise we observe at 820 nm initially the PA $S_1 \rightarrow S_n$ band of OPV₄, which decays in 0.4 ps due to the formation of the PA $S_1 \rightarrow S_n$ band of C_{60} , which has a much lower cross section. In toluene this PA C_{60} band has a long lifetime as inferred from fig. 2b. However, in odcB subsequent to this ultrafast photoinduced energy transfer, a fast intramolecular electron transfer is observed due to the stabilization of the charge-separated state by the polar medium.

A few ps after photoexcitation of C_{60} -OPV₄ in odcB a rising signal at 490 nm is observed due to ground state bleaching of OPV₄ moiety (fig. 2a) caused by an intramolecular electron transfer reaction. Moreover, at the same time an increase of absorption at the position of the OPV₄ radical cation at 820 nm is observed.⁵ After 100 ps the charge separated state disappears and we observe a negative signal, which possibly is the hot ground state obtained after intramolecular charge recombination, which decays to the ground state. These results confirm the indirect electron transfer mechanism, subsequent to singlet energy transfer in polar solvents as was predicted fluorescence quenching studies.⁵

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Room: 324–326

Photonic Analog-to-Digital Conversion

Bahram Jalali, *Univ. of California—Los Angeles, USA, Presider*

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(Invited)

1:30 pm

505-MS/s photonic analog-to-digital converter

P.W. Juodawlkis, J.J. Hargreaves, R.D. Younger, G.E. Betts, J.L. Wasserman, K.G. Ray, F.J. O'Donnell, J.C. Twichell, *Lincoln Laboratory, Massachusetts Institute of Technology, Lexington, MA 02420; Email: juodawlkis@ll.mit.edu*

1. Introduction

Optical sampling techniques^{1–3} show great promise for realizing high-resolution (12 bit) analog-to-digital converters (ADCs) with multi-gigahertz of instantaneous bandwidth. The advantages of optical sampling derive from the ultra-low timing jitter (<100 fs) of short-pulse mode-locked lasers^{4,5} and the negligible electromagnetic crosstalk between the optical sampling pulses and the electrical signal being sampled.

The phase-encoded sampling technique used in the 505-MS/s photonic ADC reported here provides high linearity³ and large suppression (50-dB) of laser amplitude noise.⁵

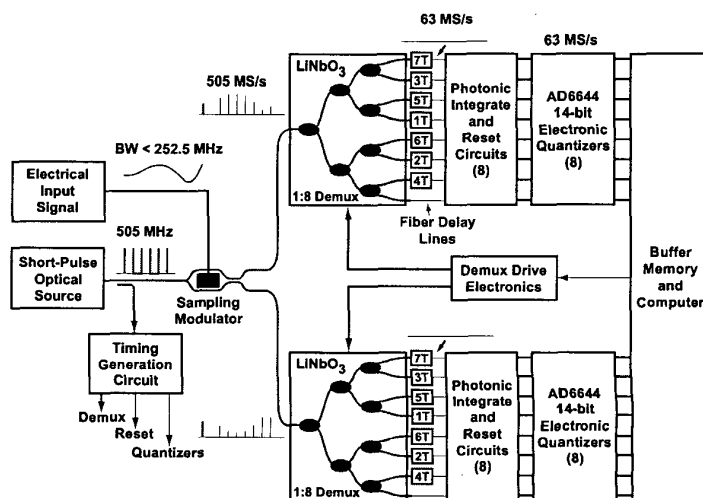
2. System description

Figure 1 illustrates the photonic ADC architecture. The short-pulse optical source is a mode-locked sigma fiber laser that is driven with 130-ps electrical pulses produced by a resonant tunneling diode (RTD) oscillator. The laser generates 25-ps pulses at the 505-MHz sampling rate. Phase-encoded optical sampling is performed via a dual-output LiNbO₃ Mach-Zehnder modulator ($V_\pi = 2.9$ V, BW = 3 GHz). A pair of 1-to-8 optical time-division demultiplexers is used to distribute the modulator's complementary output pulse streams to an array of photonic integrate-and-reset (PHIR) circuits followed by 14-bit electronic quantizers (Analog Devices AD6644) operating at 1/8 the sampling rate (63 MS/s). Fiber delay lines are used to time-align the pulses at the PHIR circuit inputs to simplify PHIR and quantizer timing. The quantized samples are calibrated, phase-decoded, and re-interleaved to produce a digital estimate of the electrical input signal.

The Ti-indiffused LiNbO₃ 1-to-8 optical demultiplexers employ a high-extinction design (Fig. 2) to minimize crosstalk between parallel channels. Each of the seven demux switch stages consists of a 1×2 switch element with an extra extinction modulator at each output arm. The stages are driven using phased sinusoids and the three elements of a given stage are driven by a common signal. The extinction for a single stage ranges between 36 and 46 dB. The bandwidth of a stage is 600 MHz. The half-wave voltages (V_π 's) vary from 6.5 to 7.4 V with <2.5% variation within a single stage. The total insertion loss for a channel ranges between 6.8 and 8.4 dB.

3. Photonic ADC performance

Initial characterization of the photonic ADC was performed by sampling a 220-MHz, 0.32- V_{pp} signal (Fig. 3). The linearity of the system can be estimated from the amplitude of the third harmonic which is 83 dB below the main tone. This



CMN1 Fig. 1. 505-MS/s photonic analog-to-digital converter system architecture.